Pd or PdO: Catalytic active site of methane oxidation operated close to stoichiometric air-to-fuel for natural gas vehicles

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ABSTRACT

A Pd catalyst supported on La-modified Al$_2$O$_3$ (La-Al) with and without doping CeO$_2$-ZrO$_2$ (CZ) is prepared via incipient wetness impregnation method. The catalysts are used as model catalyst for natural gas vehicles (NGVs) to investigate the active sites of methane oxidation within the range of air/fuel ratios (λ values) close to stoichiometric value ($\lambda = 1$). Both the two catalysts show high activity for methane oxidation under rich conditions. Under lean conditions, the methane oxidation activity over the dopant-free catalyst depend on the direction of λ change, and this catalyst displays relatively lower activity when the λ changes from richer values to lean ones. By contrast, the catalyst with dopant under the same lean conditions can nearly maintain its high activity regardless of the change direction. The results of X-ray powder diffraction (XRD) and temperature programmed reduction under H$_2$ (H$_2$-TPR) indicate the existence of the interactions between the dopant and Pd species, and these interactions are beneficial to retain Pd in oxidized state. Ex situ X-ray photoelectron spectra (XPS) experiments are explored to correlate the catalytic activity of the methane oxidation with the oxidized valent state of Pd. The results confirm that the dopant can preserve most of the Pd species in PdO even under the rich conditions. The results also suggest that both metallic Pd and PdO can act as the active sites for methane oxidation under much richer conditions, and that under lean conditions, PdO instead of metallic Pd plays a role in methane oxidation.

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1. Introduction

Automotive exhaust, as one of the sources of air pollution, contains much toxic substance such as carbon monoxide, hydrocarbon, NO$_x$ and particulate materials etc., and is arousing more and more attention. Natural gas receives increasing concern all over the world because of its widespread availability and green environmental features [1–3]. Compared to gasoline or diesel powered automobiles, natural gas fueled vehicles produce lower quantities of CO$_2$, NO$_x$ and other contaminants [4]. To meet the increasingly stringent emission regulations, however, pollutants including CO, NO and unburned CH$_4$ in the exhaust emissions of natural gas vehicles (NGVs) must be eliminated simultaneously and efficiently with

catalysts. Recently, stoichiometric NGVs are becoming dominant in natural gas heavy duty vehicles market but faced challenges [5]. Under the real working condition for NGVs, deviation from stoichiometric air/fuel (A/F) value ($\lambda = 1$) is unavoidable owing to fuel or oxygen rich during sudden acceleration as well as slowing down at any time. However, catalysts show high efficiency only in a very narrow A/F window close to λ value of 1, and a tiny deviation from the window can cause dramatically reduced catalytic activity [6–8]. Therefore, catalysts with wider operating A/F window are highly desired for NGVs. Moreover, methane is difficult to be activated [9], and efficient removal of the unburnt CH$_4$ in NGVs exhaust emissions remains very challenging [10]. Pd catalyst is currently the most efficient solution to remove CH$_4$ from NGVs exhaust emissions [11,12]. A lot of efforts were put into development of Pd catalysts for CH$_4$ oxidation under much lean conditions, and the studies found that the activity of the CH$_4$ oxidation is correlated with the oxidation state and size of Pd, and even with reaction gas compositions [13]. Besides, the active sites for the reaction are still unclear and in debated [14–16]. G. Groppi

[17] conducted comparison between the O_2-TPO profiles and the activity of CH_4 oxidation over Pd catalyst supported on La_2O_3 stabilized alumina. It indicated that metallic Pd state was much less active than PdO for CH_4 oxidation at moderate temperature. At high temperature (above 700 °C), PdO decomposes readily to metallic Pd. On this occasion, however, metallic Pd contributes CH_4 oxidation to great extent. The work suggested that the catalytic active sites for CH_4 oxidation can change between metallic Pd and PdO as the reaction temperature varies. Johan Nilsson et al. [18] performed rich (0.1% CH_4)-lean (1.5% O_2 and 0.1% CH_4) cycling experiments for CH_4 oxidation over Pd/Al_2O_3 and Pd/CeO_2 catalyst. When feed gas composition switching between net-reducing and net-oxidizing, the trend of degradation in CH_4 conversion on Pd/CeO_2 was little compared with the one on Pd/Al_2O_3. It could be attributed to the superior oxygen mobility from the CeO_2 support to Pd active sites. Recently, in situ technologies such as in situ thermogravimetry [19], in situ Raman and in situ XRD [20] were used to investigate the active sites for methane oxidation in CH_4—O_2 reaction system on Pd-based catalysts. However, the temperature ranges and reaction compositions adopted by these works on CH_4 oxidation are very different from the ones in modern NGVs [6]. Particularly, few studies about the mechanism of CH_4 oxidation operated in stoichiometric NGVs were reported.

Se H. Oh et al. [21] firstly studied methane oxidation on a CeO_2-promoted Pd/Al_2O_3 in a CH_4—CO—O_2 mixture under reducing and oxidizing conditions that are likely to be encountered in NGVs. The results showed that the Ce-containing catalyst performed a detrimental activity in CH_4 oxidation compared with the Ce-free counterpart under reducing and oxidizing conditions. Moreover, during the scan O_2 concentration from 0.2 to 1%, the Ce-containing catalyst showed inferior A/F window of activity to the Ce-free one. However, the Ce-containing catalyst can maintain a moderate activity of CH_4 oxidation under slightly lean condition, while the Ce-free catalyst showed very low activity under the same condition. Interestingly, the CH_4 oxidation activity on the Ce-free catalyst is depending on the direction of O_2 concentration change. When O_2 concentration was changed from rich to lean, CH_4 conversion close to stoichiometric CH_4/O_2 dropped rapidly. However, when the O_2 concentration change was from lean to rich, the CH_4 conversion at the same CH_4/O_2 values was much higher. The oxygen concentration hysteresis was also found over a Pd-based catalyst for NGVs [6]. However, the detailed mechanism for the phenomenon remains unclear. Notably, Klingstedt et al. [22] reported Pd catalysts on Ce-modified alumina for elimination of gas mixtures (CH_4—CO—NO—O_2—H_2O) simulating the real exhaust emissions from NGVs. They found that, during the oscillating λ scan from rich to lean conditions, the higher Ce loaded catalyst showed higher activities in conversion of CH_4 even under lean conditions (λ value up to 1.04). No work on λ scan from lean to rich conditions was presented in their paper. Both their work and the one of Se H. Oh et al. demonstrated clearly a potential of extending operating window of CH_4 oxidation to leaner conditions by adding Ce to Pd/Al_2O_3. Nevertheless, there is no answer whether Pd or PdO is the active site for CH_4 oxidation in the exhaust emission of stoichiometric NGVs. What is more, to develop catalysts with highly efficient activity for the CH_4 oxidation, investigation of the catalytic active sites under the conditions operated close to stoichiometric λ value is needed [13].

Normally, bare CeO_2 has good oxygen storage capability (OSC) but poor hydrothermal stability [23]. CeO_2-based composite oxides exhibit improved hydrothermal stability and OSC. Among them, CeO_2-ZrO_2 composite oxides [24,25] attract much attention and were usually used in commercial catalysts for stoichiometric NGVs [26]. In the present work, a Pd catalyst on a La_2O_3-Al_2O_3 support with and without doping by CeO_2-ZrO_2 composite was prepared for conversion of a gas mixture simulating the exhaust emissions

of NGVs. The catalysts were characterized by N_2 adsorption and desorption isotherms, XRD and H_2-TPR. Over the catalysts, the activity of CH_4 oxidation operated close to stoichiometric λ value was investigated under different reaction conditions such as reaction compositions and temperatures. The oxygen concentration scans coupled with ex situ XPS experiments were used to explore whether metallic Pd or PdO is the active site of methane oxidation within the λ range around 1.

2. Experimental

2.1. Support preparation

The La_2O_3-Al_2O_3 support was supplied by Rhodia company with the La/Al mass ratio of 5:95. Because the catalyst applied in NGVs is close to the engine for meeting quick cold start and will be exposed to high temperature (sometimes above 1000 °C). Thus, before the use, the support La_2O_3-Al_2O_3 composite oxides was precalcined at 1000 °C in muffle furnace for 5 h to obtain the stabilized oxides (denoted as La-Al). In the preparation of the modified support, La-Al powder was co-impregnated with the mixed aqueous solution of $Ce(NO_3)_3\cdot6H_2O$ and $Zr(NO_3)_4\cdot5H_2O$ followed by drying at room temperature for 12 h. Subsequently, dried powder was further calcined at 550 °C in static air for 3 h to get the desired modified support (denoted as CZ/La-Al) with Ce/Zr mole ratio of 1:1 and 10 wt% CeO_2-ZrO_2 content relative to La-Al.

2.2. Catalyst preparation

Using CZ/La-Al as support, a Pd-only catalyst was synthesized via incipient wetness impregnation method with the content of Pd of 6 wt% relative to La-Al. Typically, aqueous solution of $Pd(NO_3)_2$ was impregnated on the CZ/La-Al support powder following drying at room temperature overnight and calcined at 550 °C for 3 h to obtain the catalyst powder. This as-prepared powder was ball-milled with deionized water into homogeneous slurry which afterwards was coated onto honeycomb cordierite (Yixing, China, 400 cells per in^2, 2.0 cm^3). The coated catalyst was dried at room temperature overnight and then calcined 550 °C for 3 h resulting in the monolithic catalyst, Pd/CZ/La-Al. For comparison, a reference Pd sample were prepared on the La-Al support in same ways and denoted as Pd/La-Al. Each of the monolithic catalyst has the same Pd loading of about 300 g ft^{-3}.

2.3. Catalytic tests of λ operating window

Catalytic tests of λ operating window (calculated according to Eq. (1) [27]) were carried out in a home-made fixed bed reactor at atmospheric pressure and constant temperature of 500 °C. The temperature of catalyst bed was monitored with K-thermocouple. Before the tests, the samples were pretreated over the flow of industrial reaction atmospheres which is composed of CH_4 1035 ppm, NO 930 ppm, CO 4960 ppm, H_2O 10%, CO_2 10%, O_2 0.3% (λ = 0.993) and N_2 (balance) at 550 °C for 1 h. The volume space velocity was controlled in 40000 h^{-1}. After the temperature of the catalyst bed cooled to 500 °C, λ operating window tests were performed at this temperature under oscillating condition of stepwise λ range of 0.981-1.013 via only altering the concentration of oxygen from 0.043% to 0.553%. During the oscillating λ operating window tests each λ value point had a λ pulsation with an amplitude of ±0.015 and a frequency of 0.1 Hz. For the purpose of detecting the outlet emission concentration, an Antaris IGS (Thermol Fisher Scientific) was used.

$$\lambda = \frac{2\,[O_2] + 2\,[CO_2] + [CO] + [NO] + [H_2O]}{2\,[CO_2] + 2\,[CO] + 4\,[CH_4] + [H_2O]} \tag{1}$$

The conversion of reactants was calculated using the following formula:

$$X_i = 100\% \cdot (C_{i,inlet} - C_{i,outlet})/C_{i,inlet}$$

Herein, $C_{i,inlet}$ and $C_{i,outlet}$ refer to the concentration of the corresponding i species in the inlet and outlet, respectively.

2.4. Characterizations

Different reaction atmosphere experiments were operated to identify the routes of CH_4 conversion over Pd/CZ/La-Al at 500 °C, especially under net oxidizing conditions. The measurements method was conducted by oscillating λ operating tests method just as the above.

The textural properties of catalyst supports were evaluated via N_2 adsorption-desorption, operating on an automated surface area and pore size analyzer (Autosorb SI, Quantachrome, USA). Prior to operation, the samples were degassed at 300 °C for 3 h so as to remove impurities on the sample surface. The specific surface area and pore volume were calculated on the basis of BET and BJH method, respectively. X-ray powder diffraction (XRD) experiment was performed on D/Max-rA with a Cu Kα radiation (λ = 0.15406 nm) that was operated at 45 kV and 25 mA. The 2θ was scanned from 10 to 90° with an interval of 0.06°.

Reduction properties of supported Pd catalysts were assessed through H_2-TPR, performing on a home-made instrument equipped with thermal conductivity detector. To clean the surface impurities, 100 mg samples were pretreated in a quartz U-shaped tubular micro-reactor under the flow of pure N_2 at 450 °C for 1 h. Subsequently the samples cooled down to room temperature and reduction was carried out under the mixture of 5% H_2/95% N_2 with a constant heating rate of 8 °C·min^{-1}.

Varying reaction temperatures experiment was performed in order to further demonstrate the interactions between CZ and Pd. Prior to measurements, the samples were pretreated over the flow of industrial reaction atmospheres at 550 °C for 1 h and subsequently cooled to specific temperature. The measurements method was the same as the above oscillating λ operating tests.

To identify whether the valent state of Pd plays an important role in λ operating window of CH_4 especially under net oxidizing condition, the catalysts were tested by increasing the content of oxygen from 0.12 to 1.60% followed by decreasing the oxygen concentration in the opposite direction at 500 °C. During the progress, conversion of methane was calculated at the each set λ value.

The ex situ X-ray photoelectron spectra (XPS) experiments were performed on an electron spectrometer (XSAM-800, KRATOS Co.) equipped with an Al Kα radiation as a primary excitation. Binding energy was calibrated on the basis of C 1 s at 284.6 eV. For the purpose of revealing the specific chemical states of Pd species at different λ values, the samples for XPS were pretreated in the corresponding reaction atmosphere at 500 °C for 1 h. Then the reaction gases were cut off at once and the samples cooled to room temperature under inert gas (pure N_2).

3. Results and discussion

3.1. The three-way operating window tests
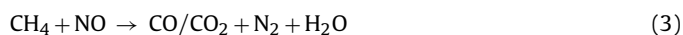
Based on this background that weak CH_4 conversion across the stoichiometric conditions (λ = 1) in stoichiometric CNG engine, reported by researchers [6–8], it is desired to develop a catalyst with wider operating A/F window for NGVs. In our work, a Pd catalyst on a La-Al support with doping by CZ composite was prepared for the operating A/F window of a gas mixture simulating the exhaust emissions of NGVs. Fig. 1 shows the typical curves of the three reac-

tants conversion versus λ value. The left side of the stoichiometric value (λ = 1) represents rich combustion, and the right lean combustion. It can be noted that both Pd/La-Al and Pd/CZ/La-Al exhibit similar catalytic activity for CO. The conversion of CO can reach almost 100% under lean condition, but slightly descends during rich condition as the λ decreases. The addition of CZ greatly improves the catalytic activity of CH_4 whose conversion is above 90% in the whole λ range investigated. In comparison, Pd/La-Al catalytic activity towards CH_4 conversion shows dramatic drop under λ > 0.995, and CH_4 conversion is only about 30% with the further increase of λ value under net-lean condition. The activity of NO conversion is consistent with the one of CH_4 conversion. Pd/La-Al exhibits complete conversion under λ < 0.992, but shows a rapid inactivation when λ > 0.995. Nevertheless, the modification of CZ is observed to be beneficial for NO conversion. Up to λ value of 1, the conversion of NO is still over 90% for Pd/CZ/La-Al, while the conversion is only about 16% over Pd/La-Al under the same conditions. However, with the continued increase in λ value under net oxidizing conditions, the conversion of NO will decline quickly.

In combination with the results of the above tests, it is necessary to make certain of the effects of CZ doping on reaction system, especially on remarkable CH_4 conversion under net oxidizing conditions.

3.2. CH_4 oxidation under different reaction atmospheres

For making sure about how CH_4 can be converted under net oxidizing conditions over Pd/CZ/La-Al, experiments using different reaction atmospheres were needed to be conducted because of the complexity of CH_4 conversion in the emissions from NGVs. Essentially, the conversion of CH_4 can occur via oxidation or partial oxidation, coupled reaction with NO, steam reforming and reforming with CO_2, as the following formula from Eqs. (2)–(5).

$$CH_4 + O_2 \rightarrow CO/CO_2 + H_2O \tag{2}$$

$$CH_4 + NO \rightarrow CO/CO_2 + N_2 + H_2O \tag{3}$$

$$CH_4 + H_2O \rightarrow CO/CO_2 + H_2 \tag{4}$$

$$CH_4 + CO_2 \rightarrow CO + H_2 \tag{5}$$

Hence, it was investigated how the removal of water and/or CO_2 from the feed influenced CH_4 conversion. The definition of λ is same as Eq. (1) mentioned above, but except the water and/or CO_2 in the formula when different reaction atmospheres were conducted. The tests were performed in the same manner towards Section 3.1 by oscillating the concentration of oxygen from 0.043% to 0.553%. Firstly, at the inlet, water from the feedstock was removed and the resulting curve showed in Fig. 2 (a). It can be found that removal of water has no detrimental effect on CH_4 and NO conversions. Interestingly, the absence of water slightly improves the conversion of CH_4, indicating under net oxidizing conditions the existence of water in the reaction system may hinder CH_4 conversion to some extent. However CO conversion descends remarkably, especially during rich conditions in the absence of water. This suggests that water gas shift reaction distinctly promotes CO conversion under rich conditions if water exists at the inlet [28,29]. Fig. 1(b) and Fig. 2(b) demonstrates that whether CO_2 exists in the feedstock or not can hardly influence the trend of the three-way λ operating window. But there is no denying that CH_4 steam or dry reforming can both proceed in the reaction system. Interestingly, even in the absence of O_2 (as shown in Fig. S1), the two reforming reactions make crucial contribution to the complete conversion CH_4, which is in accordance with the observation in literature [12,30]. In connection with Fig. 2a and b, on one hand, it could be understood CH_4 steam or dry reforming would promote CH_4 complete conversion in the very rich conditions. On the other hand, with the increase
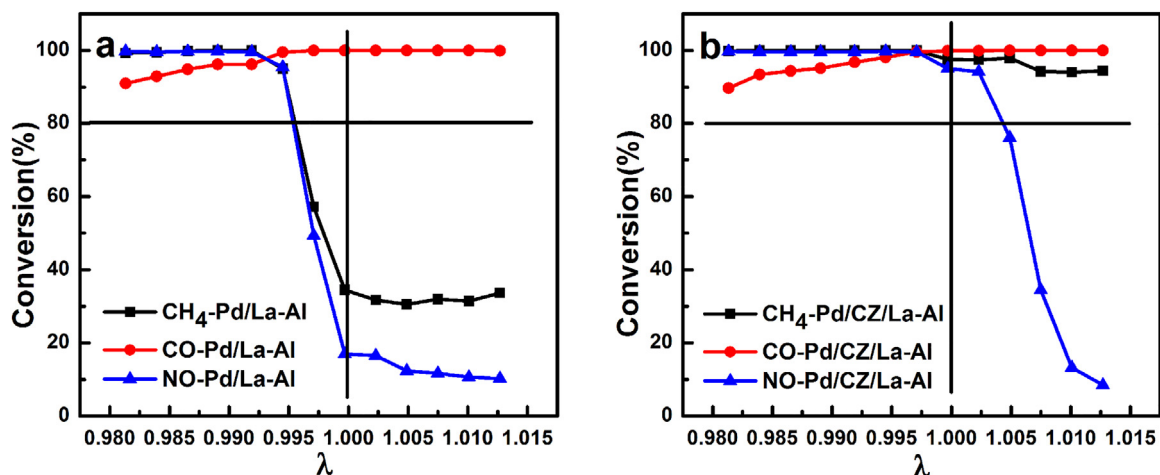
Fig. 1. λ operating window measurement results corresponding to Pd/La-Al (a), Pd/CZ/La-Al (b). Conditions: 500 °C, CH_4 1035 ppm, NO 930 ppm, CO 4960 ppm, H_2O 10%, CO_2 10%, varied O_2 content and N_2 (balance).
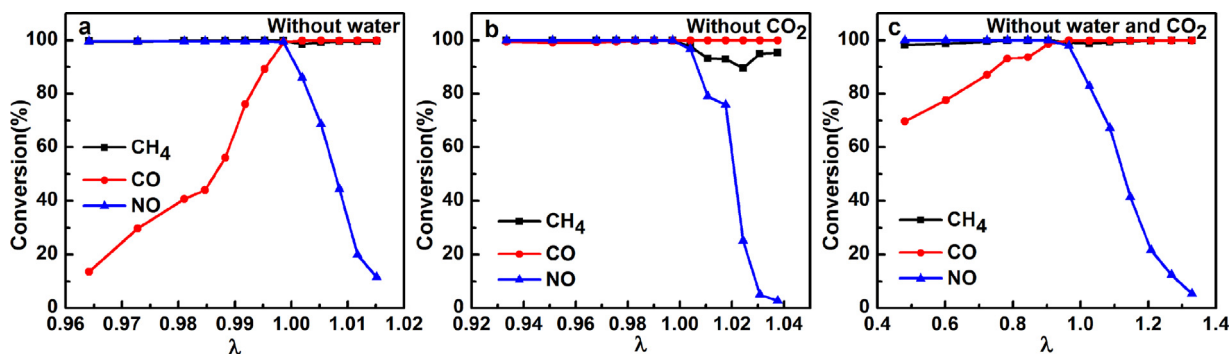
Fig. 2. λ operating window measurement results of the Pd/CZ/La-Al catalyst under different reaction atmospheres in the absence of water (a), CO_2 (b), water and CO_2 (c). Conditions: 500 °C, oscillating λ tests in similar atmosphere as Fig. 1.

of λ value, CH_4 steam or dry reforming becomes more and more uncompetitive and inferior to CH_4 oxidation [13,31]. Eventually when water together with CO_2 were removed from the feedstock, the result shows the trends of CH_4 and NO are nearly consistent with the curve where the feedstock is only free of water. Note CH_4 conversion in the very rich conditions even keeps complete conversion in the absence of water and CO_2 in the feed. Under the circumstance, CH_4 can be converted through CH_4 oxidation and coupled reaction with NO. At the same time, CH_4 decomposition ($CH_4 \rightarrow C + 2H_2$) along with CO disproportionation ($2CO \rightarrow C + CO_2$) are likely to occur. On this occasion, CH_4 dry reforming occurs readily to sustain CH_4 high conversion owing to the generations of CO_2 through the CO disproportionation. The formed carbon deposition was observed to be located on the surface of the monolithic catalyst [32]. The carbon deposition would lead to catalyst deactivation and unsteady behavior of the system, especially under the very rich conditions. However, from Fig. 2c, the effects of carbon deposition on the test seem to be insignificant. Notably, the formation of carbon deposition could be hindered remarkably with the gradual increase of oxygen content in the feed and water vapor formed [32]. Moreover, with the increasing λ across the stoichiometric condition, CH_4 oxidation compared to steam or dry reforming would become the dominant reaction to contribute the complete conversion of CH_4 [13,31]. In addition, as can be seen from Fig. 1b, NO conversion decreases sharply when $\lambda > 1$, indicating that the coupled reaction between CH_4 and NO can hardly proceed under $\lambda > 1.01$ (Fig. 1(b)). In short, considering the reactions in which CH_4 can participate, it may be concluded that the conversion of CH_4 mainly proceeds through oxidation path when oxygen is excess. It is needed to fur-

Table 1
Specific surface areas, pore volumes and average pore radii of the samples.

Samples	S_{BET} (m^2 g^{-1})	V (ml g^{-1})	R (nm)
La-Al	128	0.54	8.5
CZ/La-Al	118	0.49	8.2

ther figure out why the doping of CZ can enhance CH_4 oxidation under net oxidizing conditions.

3.3. The effect of CZ dopant on the textural properties and structural properties of the catalyst

With the purpose of identifying whether CZ dopant can change the textural properties of the catalyst to have influence on the three-way catalytic activity window, N_2 adsorption-desorption experiment for the catalysts was performed. Both adsorption-desorption isotherms and pore-size distributions of support display almost the same results for the two supports (shown in Fig. S2). The results suggest that the CZ doping does not change significantly the textural properties of the support. It can also be found that doping of CZ slightly decreases specific surface areas compared to those undoped counterpart (Table 1). Nonetheless, with a view to the λ operating window measurement where the CH_4 conversions over the catalyst with and without CZ doping are very different, slight reduction of specific surface area seems insignificant to the differences. Therefore, the textural properties of catalyst would play a minor role in CH_4 oxidation in the working window.
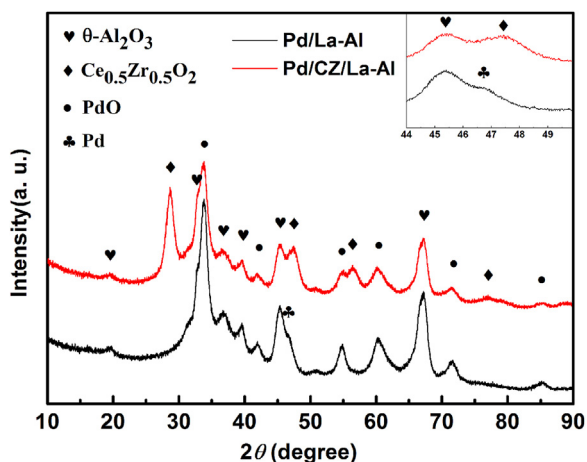
Fig. 3. XRD patterns of Pd/La-Al and Pd/CZ/La-Al.

Fig. 4. H_2-TPR profiles of the Pd/La-Al and Pd/CZ/La-Al.

Table 2
H_2 consumption and temperature of TPR peaks for catalysts.

Samples	H_2 consumption ($\mu mol/g_{cat}$)	Peak temperature (°C)	Theoretical H_2 consumption[a] ($\mu mol/g_{cat}$)
Pd/La-Al	152.4	103	531.8
Pd/CZ/La-Al	320.8	104	488.6

[a] Theoretical H_2 consumption for only PdO reduction.

Fig. 5. CH_4 conversion versus λ value for Pd/CZ/La-Al at 500 °C, 450 °C and 400 °C. Conditions: oscillating λ tests in the atmosphere as Fig. 1.

The XRD patterns of the powder catalysts are shown in Fig. 3. The most diffraction peaks of both samples are consistent with the characteristic peaks of monoclinic θ-Al_2O_3 (PDF-ICSD79-1559) and tetragonal PdO (PDF-ICSD43-1024). For both samples, the characteristic peaks corresponding to La_2O_3 are not detected. The absence of the characteristic La_2O_3 peaks may be caused by its good dispersion on the support. These results are in good agreement with the ones [33,34]. Together with the θ-Al_2O_3 and PdO diffraction peaks, the doped samples show tetragonal $Ce_{0.5}Zr_{0.5}O_2$ (PDF-ICDD38-1436) diffraction peaks that are consistent with the literature reported [35]. It can also be observed that doping of CZ can weaken the intensity of PdO in contrast with the undoped counterpart. It indicates modification by CZ doping can suppress the crystallinity of PdO, and thereupon the dispersion of PdO species can be further promoted compared with the counterpart free of CZ, which is in line with the literature [22,36]. This can be evidenced based on Pd mean particle size data (shown in Table S1) from XRD spectra and TEM tests (Fig. S3). More importantly, Pd/La-Al shows metallic palladium diffraction peak at $2\theta = 46.6°$ (from the inset in Fig. 3). In contrast, CZ doping effectively suppresses the existence of metallic palladium peak, suggesting that more Pd species may maintain the oxidized state which is regarded as the active phase for CH_4 oxidation [37,38]. Therefore, how the doping of CZ changes the electric state of Pd element resulting in a wider operating window for CH_4 oxidation, especially under net oxidizing conditions, is needed to be further explored.

3.4. The reducibility of the catalyst

H_2-TPR experiments can be conducted to study the reducibility of Pd-supported catalysts, which might suggest the interaction between Pd and support. For investigating the reducibility of the catalyst before and after CZ doping, H_2-TPR experiments of the Pd-supported catalysts were explored and the results showed in Fig. 4. In the case of Pd/La-Al, the TPR profile exhibits two peaks which consist of one positive peak (103 °C) and one negative peak (80 °C). The peak at 103 °C represents the reduction of PdO species finely dispersed on Al_2O_3, and the negative one at 80 °C attributes to the decomposition of palladium hydride [39–41]. Compared to Pd/La-Al, Pd/CZ/La-Al displays the similar trends which show one positive peak (104 °C) and one negative peak (74 °C). The peak of hydrogen consumption for Pd/CZ/La-Al at 104 °C attributes to the reduction of PdO species as well as Ce^{4+} that is in close contact with Pd. From Fig. 4 and Table 2, it can be clearly seen that Pd supported on La-Al support modified by CZ possesses twice much more H_2 consumption than Pd/La-Al, evidencing the strong interaction
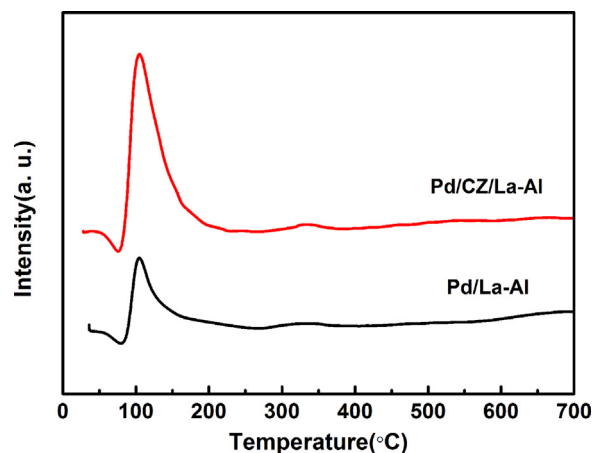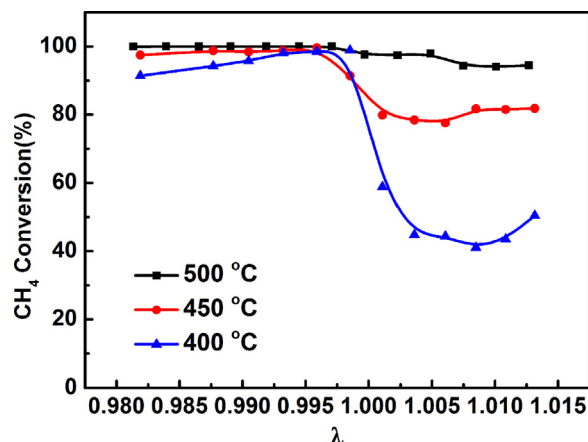
between Pd and Ce-Zr-O. The absence of any hydrogen reduction peak for cerium oxide at higher temperature further confirms the existence of the interactions as reported in the literature [42]. The interactions can promote the mobility of active oxygen between Pd and Ce. As a result, CZ may affect the electric state of the Pd species which would prefer in form of PdO during CH_4 oxidation on Pd/CZ/La-Al.

3.5. The effect of varying reaction temperatures

In order to further investigate the interactions between CZ and Pd, the influence of varying reaction temperatures (400, 450 and 500 °C) on the activity of CH_4 oxidation was studied (Fig. 5). For different reaction temperatures, CH_4 oxidation under rich conditions shows almost no difference at different λ value. But, with oxygen content being excess (λ > 1), the lower reaction temperature causes much lower conversion of CH_4. This is concluded that water inhibits CH_4 oxidation on Pd-based Ce-containing catalyst
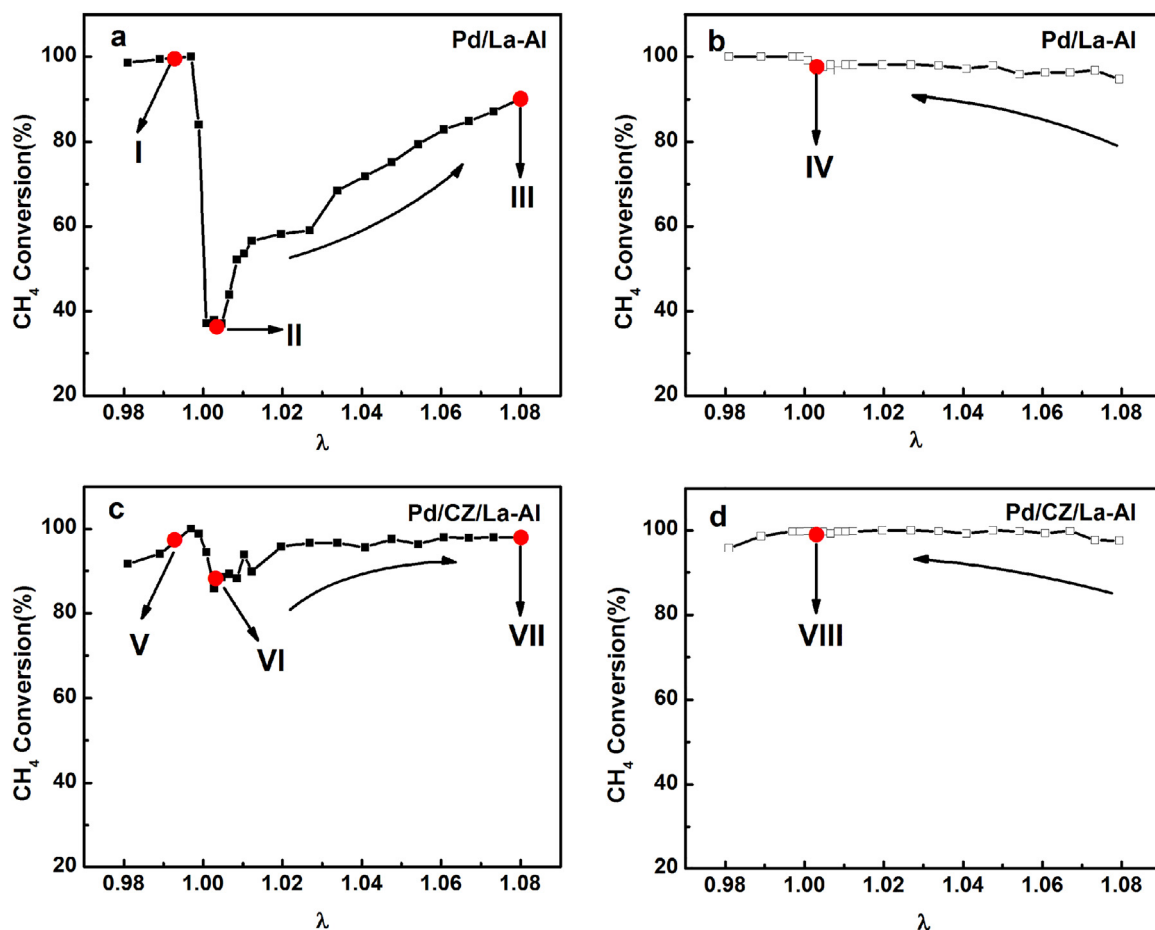
Fig. 6. CH$_4$ conversion over Pd/La-Al (a and b) and Pd/CZ/La-Al (c and d) at the increase (filled symbols) and subsequent decrease (open symbols) of λ value. Conditions: 500 °C, stationary λ measurements in reaction atmospheres as Fig. 1.

under lean conditions [43]. The poisoning effect of water under lean conditions is due to the formation of stable OH groups on the surface of ceria and Pd nanoparticles [44]. These OH groups covering on the ceria surface inhibit oxygen mobility from ceria to Pd, hindering CH$_4$ oxidation under lean conditions. Nevertheless the presence of hydroxyl exerts minor side effect on CH$_4$ oxidation with the increase in temperature [44]. It can be due to higher temperature making desorption of OH from the surface easier, accelerating oxygen mobility between CZ and Pd. Thus, under lean conditions, water hinders the interactions between CZ and Pd to some extent, and these interactions can recover by increasing temperature. Farther whether these interactions affect the oxidized state of Pd, producing difference in CH$_4$ conversion compared to the one undoped, is answered through the following hysteresis studies coupled with XPS experiment.

3.6. Oxygen concentration hysteresis studies

To clarify the role of CZ modification in CH$_4$ oxidation over Pd-based catalyst, we conducted oxygen concentration hysteresis experiments at 500 °C. Fig. 6 shows the curves of CH$_4$ conversion versus λ value, which were measured by changing oxygen concentration from different directions at 500 °C. For Pd/La-Al, starting from rich conditions and progressively increasing oxygen concentration up to a certain extent (λ = 0.993), nearly 100% conversion of CH$_4$ can be obtained. Soon afterwards, the further increment of oxygen content (λ = 1.003) leads to a sharp deactivation of CH$_4$ activation (about 35% conversion). However, with the further increase in oxygen concentration, CH$_4$ conversion raises steadily and even-
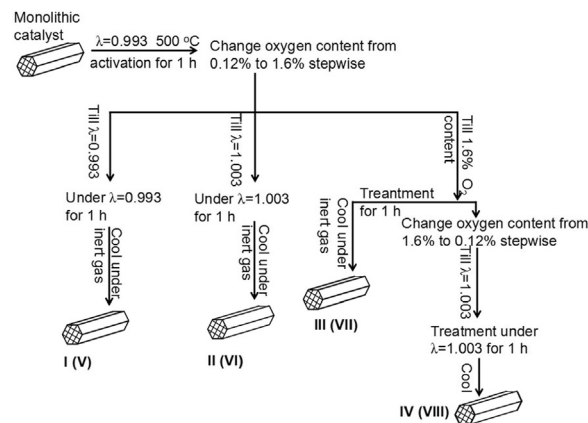

Fig. 7. Schematic preparation of the samples for XPS tests.

tually up to 90%. But unlike the profile of gradually increasing oxygen concentration, decreasing oxygen content from 1.60 to 0.12% gradually does not cause deactivation in CH$_4$ activation, and CH$_4$ conversion is always high in the whole λ value range (beyond 90%). Nevertheless, under net oxidizing conditions, the CH$_4$ conversions at the same λ value show remarkable differences depending on the direction of changing λ value. Particularly, at λ = 1.003, the conversion of CH$_4$ in the change from lean to rich is 60% higher than the one in the change from rich to lean. As Pakharukov et al. [45] reported, for Pt-catalyzed CH$_4$ oxidation in the CH$_4$–O$_2$ system, a same hysteresis phenomenon happened. It was found that
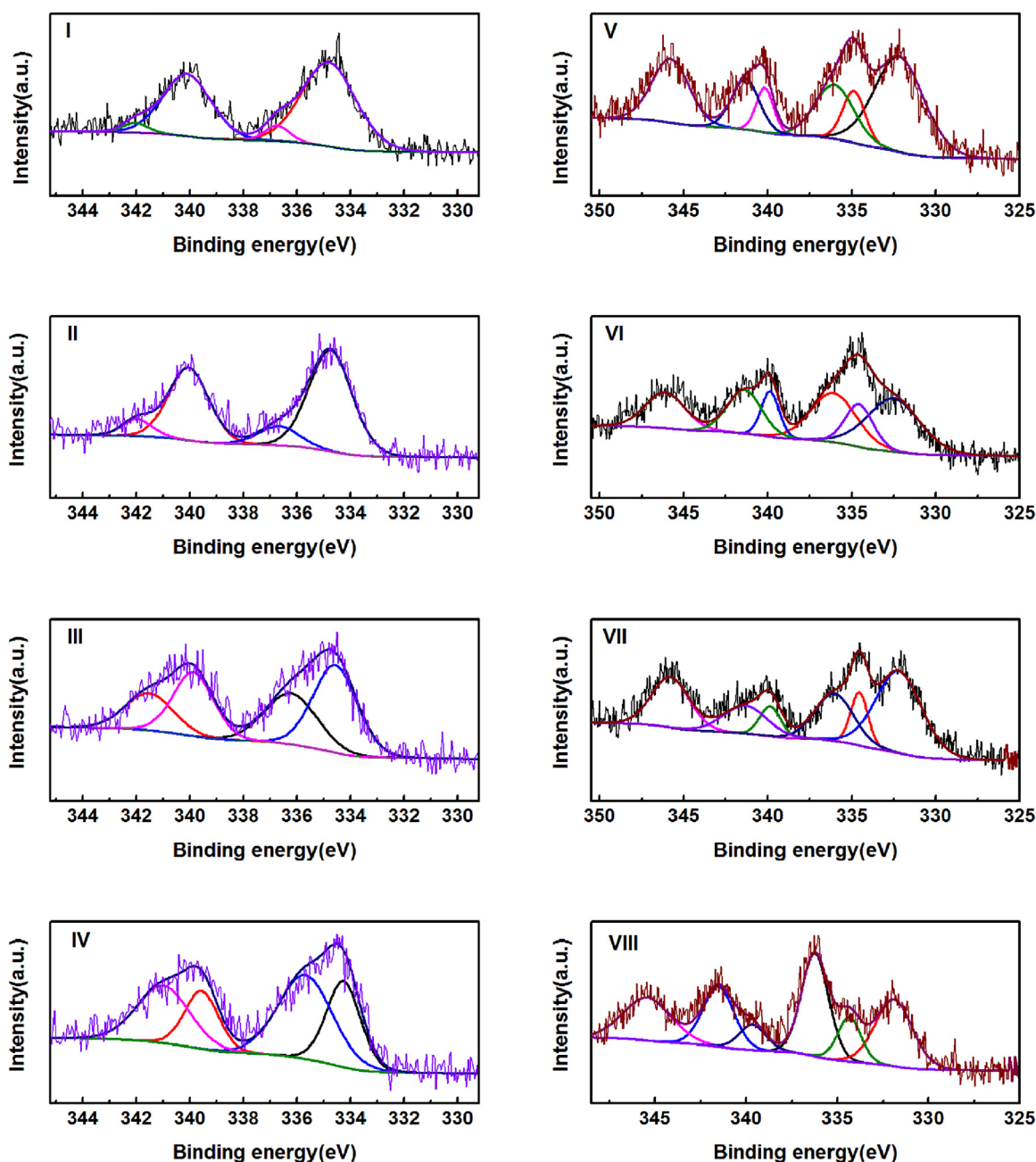
Fig. 8. The X-ray photoelectron Pd 3d and Zr 3p spectra of Pd/La-Al and Pd/CZ/La-Al under different reaction states. Relevant reaction states were marked corresponding to the red point shown in Fig. 6. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

two stable stationary states of Pt with different activity under the same conditions depending on the direction of the change in the O_2/CH_4 ratio. In situ X-ray photoelectron spectroscopy correlated the changes in the oxidation state of Pt with the activity in CH_4 oxidation. Thus, it seems that a change in the valent state of palladium during the λ sweep may occur and account for the hysteresis phenomenon in our experiments [6,21].

For Pd/CZ/La-Al, when starting λ sweep from rich to lean, the trend of CH_4 conversion is completely different from that for Pd/La-Al. Although the initial increment of oxygen concentration produces fluctuation in CH_4 conversion, the valley value located at λ = 1.003 is still over 87% which is higher than Pd/La-Al (35%) under the same conditions. The further increase in the oxygen content improves CH_4 conversion all the way. In view of Pakharukoví's stud-

ies, the reasons for maintaining catalytic activity in CH_4 oxidation during the progress of increasing λ value can be that the CZ doping can effectively preserve the oxidation state of palladium. Interestingly, during the opposite direction of changing oxygen content, Pd/CZ/La-Al behaves steadily with high CH_4 conversions which are similar to those obtained during the same change direction over Pd/La-Al.

To further identify whether the valent states of Pd exert remarkable different CH_4 oxidation behaviors under the same conditions, ex situ X-ray photoelectron spectra experiments were conducted on both Pd/La-Al and Pd/CZ/La-Al powder samples which were tested at different λ values (point I to point VIII shown in Fig. 6). The samples for the XPS test were prepared according to the procedures shown in Fig. 7.
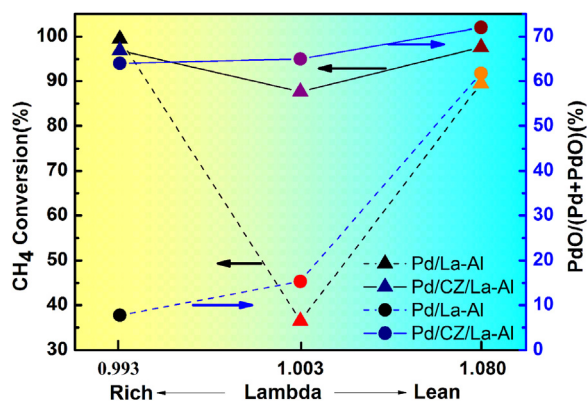
Fig. 9. The ratio of PdO/(Pd + PdO) and CH$_4$ conversion at different λ values.

3.7. Ex situ X-ray photoelectron spectra

For Pd/La-Al catalyst, it can be noted from Fig. 8 that when initially increasing the oxygen content to point I (λ = 0.993), the analysis of photoelectron Pd 3d$_{5/2}$ spectra of point I (active state) shows that the overwhelming majority of surface palladium element exists as Pd^0 (334.8 eV) and only 7.8% PdO (336.7 eV) remains according to the PdO/(Pd + PdO) ratio shown in Fig. 9. However, with the increase in oxygen content to point II (λ = 1.003), the active state in CH$_4$ conversion changes sharply to an inactive state with very low CH$_4$ conversion. The resulted XPS data (point II) are similar to that of point I though percentage of Pd^0 slightly decreases (84.7%). When much more oxygen (λ > 1.003) entering into the reaction system, it can be observed that most of metallic palladium can be gradually oxidized into PdO species at point III (61.9%) with a significantly increased CH$_4$ conversion. The results suggest that the activity of CH$_4$ conversion depends on the Pd/PdO ratio and that the active site for CH$_4$ conversion may be changed at different λ values. Under net rich conditions, metallic Pd as dominant Pd species exhibits high activity for CH$_4$ conversion despite some of its surface being covered by oxygen. When the oxygen concentration increases to point II (λ = 1.003), some metallic Pd species are oxidized into PdO. Nonetheless, due to "oxygen poisoning" [21], the surface of the remaining metallic Pd may be fully covered by oxygen. Under this circumstance, adsorption and activation of CH$_4$ molecules on metallic Pd can hardly occur [46]. Fortunately, PdO can display activity for CH$_4$ conversion at λ = 1.003 (comparison between point II and IV). However, the CH$_4$ conversion is low at point II (λ = 1.003) because of low amount of PdO (15.3%). Hereafter, more PdO are formed from oxidation of metallic Pd as the oxygen concentration increases from point II to III. As a result, the CH$_4$ conversion increases steadily. Interestingly, when oxygen content decreases from lean to point IV, 59.3% of superficial Pd species are PdO. The value is prevailing over the one of the point II (only 15.3%). Consequently, CH$_4$ conversion at point IV is much higher than the one at point II.

With regard to Pd/CZ/La-Al catalyst, Fig. 8 shows the significantly different ratio of Pd and PdO species in compared with that of Pd/La-Al. The reason for such behavior may be due to the easier mobility of active oxygen of support to Pd after CZ modification, which may mean the differences of CH$_4$ activity between the two catalysts promoted or unpromoted by CZ. Specifically, when the oxygen content gradually increasing to a certain level (point V, λ = 0.993), the corresponding XPS results of Pd 3d$_{5/2}$ show that more PdO (336.2 eV) exists than metallic Pd (334.8 eV). The ratio of metallic Pd (35.9%) to PdO (64.1%) at point V is very different from the one at point I where metallic Pd is the dominant Pd specie. In general, CZ doping can be favorable to maintain the oxidized states of Pd under reaction conditions, and results in appropriate distribution

of Pd and PdO active site pairs for CH$_4$ oxidation [47,48]. Thus, both Pd and PdO at point V synergistically contribute to the CH$_4$ oxidation with a high conversion (96.9%). Then, oxygen content further increases to the activity state of point VI (λ = 1.003) where the relative percentages of metallic Pd and PdO do not change significantly. XPS data exhibit 65% Pd species on the surface of catalyst in PdO state (336.1 eV). On this occasion, the conversion of CH$_4$ declines slightly to 87% which is still much higher than the one at point II (36.5% conversion) where the amount of PdO is much lower (15.3%). The slight decrease may be due to the inactivation of some metallic Pd which is fully covered with oxygen under the lean condition. Interestingly, further increment of the oxygen concentration from point VI to VII almost recovers the CH$_4$ conversion to the initial level (about 97.6%) rapidly, mainly owing to that more PdO is formed with the increase of oxygen (Fig. 9). During changing the oxygen concentration from lean to rich, all the CH$_4$ conversions at different λ values are high (about 95.8-99.8%). However, the CH$_4$ conversions under lean conditions are slightly higher than the ones under rich conditions, which may be due to the transformation of some PdO to Pd. It is worth noting that the amount of PdO (72.6%) at point VII is higher than the one at point III (61.9%). The result further confirms that CZ doping is helpful to maintain Pd species in PdO. In summary, due to the good interaction between Pd and Ce-Zr-O, the mobility of active oxygen from CZ to Pd can readily achieve the goal of facilitating the stability of PdO species regardless of rich conditions or lean conditions. In the whole of λ range across the stoichiometric conditions, CZ modification can maintain roughly 64% superficial Pd element in PdO state. Even though metallic Pd or PdO species can both contribute CH$_4$ conversion significantly under rich conditions, once moving to net oxidizing conditions, just PdO species promoted by CZ doping would achieve full conversion of CH$_4$. Consequently, CH$_4$ active conversion state can be always arrived no matter what the reaction atmosphere is rich or lean. In contrast, Pd/La-Al conversion is easily affected by reaction atmosphere (lean or rich) and direction of O$_2$ concentration change, essentially due to its poor ability to transform Pd to PdO.

4. Conclusions

In summary, Pd/La-Al modified by CZ can remarkably enhances CH$_4$ oxidation around the stoichiometric value than that of Pd/La-Al. The hysteresis studies coupled with the XPS data suggest that higher proportion of oxidized palladium can account for the improvement of CH$_4$ conversion. The results demonstrate that both metallic Pd and PdO are the active sites for CH$_4$ oxidation under richer conditions (λ < 1), and that under lean conditions (λ > 1), PdO plays a dominant role in methane activation. In addition, with the CZ modification, the A/F window of NO can also be enhanced to some extent compared to Pd/La-Al catalyst. This could be ascribed to more oxygen vacancies formed by palladium-cerium interactions helping the NO dissociated adsorption [49]. However, the NO conversion still drops sharply under λ > 1. The studies regarding to effectively widening the operating window of NO to much leaner conditions are still needed to be devoted.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2017.07.037.

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